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SUPERCONDUCTOR MATERIALS. A COMPARISON OF SELECTED STRATEGIC MATERIALS TECHNOLOGIES IN THE U.S. AND U.S.S.R

Battelle Columbus Laboratories

Prepared for:

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April 1973

A Comparison of Selected Strategic Materials Technologies in the U.S. and U.S.S.R.

SUPERCONDUCTOR MATERIALS

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Sponsored by
Advanced Research Projects Agency

ARPA Order No. 2371

METALS AND CERAMICS
INFORMATION CENTER

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FOREWORD

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The research was carried out under Program Code Number S3608A by Metals and Ceramics Information Center (MCIC), with H. D. Moran (614—299-3151, X3471) as Program Manager, and K. R. Hanby (614—299-3151, X1784) as Principal Investigator. Modification P00002 of MCIC's base contract covered a task for ARPA that involved preparation of this report plus four others of a similar nature. In the amount of $50,662, the Modification was effective between January 15 and May 31, 1973.

DISCLAIMER

A Comparison of Selected Strategic Materials Technologies in the US and USSR

SUPERCONDUCTOR MATERIALS

TECHNICAL SUMMARY

The use of superconductive materials in rotating electrical machinery would permit a considerable reduction in equipment size, which would be especially useful for naval applications. All of the known materials for such applications, however, must be maintained at temperatures below 20 K (-253 C) in order to keep them in the superconductive state. Materials of construction for equipment used to maintain cryogenic temperatures must be sufficiently ductile at those temperatures to avoid brittle failures in service. Research and development on superconductive machinery, including choice of materials of construction (or development of such materials) is underway in the United States, primarily under sponsorship by ARPA. The objective of the work described in this report was to determine the status of similar work in the USSR. A survey of Soviet research aimed at discovering materials that are superconductive at temperatures above 20 K was included, as such materials obviously would be very useful anywhere. The method of approach was to survey systematically the recent Soviet literature.

The results of the survey indicated that in basic research related to superconductive materials, Soviet efforts have paralleled ours. In view of apparently decreasing US efforts in such basic studies, the Soviet relative position is likely to grow stronger. In actual experimental application of these materials, the Soviets seem to be somewhat behind us. There was no indication that the Soviets have discovered any new materials with high (above 20 K) temperatures of transition to the superconducting state.

The patterns of Soviet and US development of constructional metals and alloys for cryogenic applications are quite similar. The Soviets have a temporary lead over us in the cryogenic application of manganese-nitrogen containing stainless steels, which they have investigated systematically. The Soviets also were the first to specify a titanium alloy for cryogenic superconducting machinery applications.

The present report emphasized superconductive materials for use in rotating electrical machinery. Future studies might be concentrated on application of superconductors in power transmission, electromagnetic-shielding, or other applications. The present report should be updated regularly, since the indications are that both US and Soviet researchers are actively pursuing the subject. Maintenance of an awareness of worldwide activities on the development of high transition temperature superconductive materials would appear to be particularly worthwhile.

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V. E. Wood

SUMMARY

Serious thinking about the applications of superconductivity began in the USSR at about the same time as in the US, and the Soviets have continued strong in superconductivity theory. During the decade of the 1960's, however, they fell far behind the US in the experimental area of superconducting materials, despite a sizable research effort, and they are only now beginning to catch up. While some Nb_3Sn ribbon was available in the USSR as early as 1961, great difficulties have been experienced there in producing such materials in commercial quantities. The only real fundamental advance in superconducting materials made in the USSR during the 1960's was Alekseevski's discovery that Nb_3Al-Nb_3Ge solid solutions had higher transition temperatures than Nb_3Al alone. And of course it remained for Matthias and coworkers to demonstrate that the transition temperature could be raised to above 20 K. One can only guess at the reasons for the general lack of innovative success in the USSR; our guesses are

(1) Insufficient attention to details of preparation techniques and failure to apply modern materials characterization methods, and

(2) Lack of close cooperation between theorists and experimenters.

These are facile suggestions of course, but analysis of the literature pretty strongly indicates their validity.

In the past 2 or 3 years this situation seems to have changed somewhat. There has been a great deal of systematic Soviet research on superconducting materials of greatest interest for technological applications and on related materials. The Soviets now claim that good Nb_3Sn ribbon can be prepared by several methods, and V_3Ga ribbon is also being studied. Systematic metallurgical studies of alloys of niobium with Group IVA elements are being carried out by several groups; several

papers on high-transition-point ternaries have appeared; much theoretical and experimental work on cladding of superconducting wires is being done, and the factors controlling critical current density are being intensively studied at a fundamental level.

Meanwhile, US researchers (and perhaps even funding agencies) apparently have been reducing the extent of studies in these areas in favor of what they believe are more promising fields. It may be that US work is just becoming more proprietary, and is thus not showing up as much in places like the APS Bulletin or Abstracts of LT13. To be sure, past US superconductor research has been quite effective. The most important recent advance in A15-type compounds, the production of Nb_3Ga with transition temperatures in excess of 20 K, was made in the US. Further, should Heeger's claim* of superconductivity at about 60 K in fulvalene-TCNQ** hold up and lead to some sort of practicable material, the US very broadly based materials approach will have more than justified itself.

One should bear in mind that it may well turn out that superconductive materials (and material preparation processes) now available are entirely good enough for most applications of interest, and not much future research will be necessary by either the US or the USSR. On balance, it seems that if significant further advances exist to be made in these materials, right now the Soviets are a little more likely to make them.

There is very little published Soviet experimental work on novel methods of obtaining higher transition temperatures, but there is little doubt they have started working on intercalation materials, sandwich-type setups, long chains, and perhaps others. In most of these efforts, they appear to be the followers rather than the leaders, despite the theoretical preeminence of V. I. Ginzburg in the high transition temperature area. It appears doubtful that the Soviets have anywhere near the financial support that US investigations of high transition materials enjoy at present.

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*"Claim" is a bit too strong a word, but we don't know what else to call it.

**A. J. Heeger, post-deadline paper at American Physical Society Meeting, San Diego, March, 1973.

INTRODUCTION

This report presents a comparative assessment of US and Soviet capabilities in certain aspects of superconducting materials. Advances in materials of types likely to find application in devices, particularly in electrical machinery, and developments of high-temperature superconductors have been emphasized, nearly to the exclusion of other topics. This choice is in accord with our understanding of the principal interests of the ARPA sponsor. The report also describes our attempt (not entirely successful) to find out what specific superconductive materials are being considered for given applications in the USSR and what the Soviets believe the problems connected with the use of these materials to be.

The primary consumers of the present report are assumed to be at least as familiar with current US work as we; therefore the report emphasizes recent Soviet work. The principal source of information was published Soviet literature back to January, 1970, which is catalogued in an information-retrieval system available at Battelle-Columbus. Since the computer search was found to cut off fairly early in 1972, we brought the survey more up to date by scanning recent issues of abstract journals and of Soviet publications likely to contain articles on superconductivity; this could not be done in an entirely systematic way, but we tried to cover the "quality" journals at least.

The more than 900 abstracts of the computer-generated references were reviewed, and about 150 were found to be fairly relevant to the present study. Full texts that were available at Battelle-Columbus for the most relevant of these have been examined. The present report summarizes the results of that examination, and includes description, in some cases, of computer-generated abstracts for which the full text was not available. Classified information was examined during the information-collection phase of this study. We do not believe that it contributed sufficient information to warrant making this study classified; therefore, it is not included here.

The reader should bear in mind that long publication lag times and delays in receipt of journals mean that he generally is getting a picture of Soviet work that is at least 1-1/2 to 2 years old.

CONCLUSIONS

1. The Soviets have used pure niobium, Nb_3Sn, and various niobium alloys in superconducting applications within electrical machinery. They are somewhat behind the US in actual experimental application of superconductors in machinery; however, in the theory and design areas, they are on a par with the US.

2. The Soviets have not studied cladding systematically until fairly recently. Copper cladding is the standard in the USSR as in the US. No evidence of Soviet work on cupronickel or aluminum cladding was found. Comparison with recent US work is difficult because of the probable proprietary status of significant cladding developments.

3. In the development of superconductive materials of A15 structure, the Soviets were far behind during the 1960s, but now have nearly caught up with the US. Increased Soviet activity coupled with decreased US activity gives the Soviets the edge for future developments in this area.

4. The USSR is presently somewhat ahead of the US in experimental work on developing ductile niobium alloys. However, there seems to be a decreasing effort in this area on the part of both countries, possibly because their needs are met by keeping up with results of research in the UK and West Germany.

5. Efforts to develop "high-temperature" superconductors are underway in both the US and USSR. Further development in this area depends upon breakthroughs, hence is difficult to predict and to compare the efforts.

6. Because of the general decrease in US research effort on superconductive materials, on balance, if significant future advances are to be made, the Soviets are a little more likely to make them.

GENERAL BACKGROUND

The putative advantages of using type-II semiconductors in electrical machines are[1]

(1) Low power consumption (even including power required for refrigeration to maintain the superconductive state)

(2) Compactness, and

(3) Greater output power for given strength of rotor.

The disadvantages are

(1) High initial cost, and

(2) Necessity of refrigeration, with concomitant possibilities of new failure modes.

The qualities desired of the superconductor in such applications are[1]

(1) High transition temperature, T_c, to reduce refrigeration costs and generally to lead to improvements in other parameters,

(2) High critical field H_c (generally H_{c2}), so that large currents will not drive the superconductor normal,

(3) High critical current density J_c, for maximum power output per amount of wire,

(4) High stability against sudden changes in external conditions, usually achieved by cladding and embedding, and

(5) Low ac loss. (Even though it will be generally preferable to avoid hysteresis losses by using dc in field windings, rather than ac in armatures of electrical equipment,[2] the superconductor is bound to experience some ac fields; there are applications, such as transformers, where this is inevitable.)

The obtaining of a high J_c, which is the primary (but not the only) goal in developing superconducting materials for most applications, depends on pinning of flux lines by dislocations, impurities, second-phase precipitates, or other inhomogeneities, and thus on the history of metallurgical treatment of the specimen. This treatment of course not infrequently influences the composition of the superconducting state itself, complicating interpretation of experiments somewhat.

One can obtain some idea of the Soviet position in superconducting materials and devices as of 2 to 8 years ago by perusing some recent books on the subject. In particular, we have looked at*

(A) "Proceedings of LT10" (4 volumes, Moscow 1966)[3]--old, but illustrative of the best Soviet work of that time.

(B) "Physics and Metallurgy of Superconductors" (Consultants Bureau translation, 1970, of 1965-66 conference proceedings)[4]

(C) "Problems of Superconducting Materials" (Moscow 1970)[5]

(D) "Questions of the Application of Super-Low Temperatures in Electrical Engineering" (Leningrad, 1971)[6]

(E) "Superconducting Alloys of the System Nb-Ti-Zr-Hf" (Moscow, 1971)[7]

(F) "Superconductivity in Marine Technology" (Leningrad, 1971)[8]

The last four references are discussed further below. Pertinent recent Western references are

(G) Proceedings of IEEE special issue on applications of superconductivity (1973)[9]

(H) Certain articles in the AIP Conference Proceedings volume "Superconductivity in d- and f-band Materials" (1972)[10]

(I) The huge two-volume treatise "Superconductivity", (1969)[11] and the review article of Dew-Hughes[1] already referred to.

In reading through these volumes, one is struck by how little reference there is to Soviet experimental work in <u>either</u> the Soviet or Western volumes. One looks in vain in the Soviet volumes for much discussion of such topics popular in Western work of the time as the "critical" state; flux jumping, flow, creep, and pinning; the fluxon lattice; paramagnetic limits on H_{c2}; or ac loss mechanisms. What one does find mostly, as far as experimental work goes, is a great deal of conventional metallurgy and a lot of tests (J_c, H_c, T_c) on standard-alloy wires in various configurations. Of course, this selection of references is somewhat biased toward near-term applications, and a survey of JETP (Soviet Journal of Experimental and Theoretical Physics), for instance, would give a somewhat different picture, but it does give some idea of the problems that the Soviets considered important (or maybe accessible) at the time. To a large extent this attitude has persisted, but with some important modifications, as will be described below.

*Complete bibliographic data in references.

Since the last 4 Soviet references may not be easily available, a few words about them might be appropriate. (C) consists of selected papers from the 5th National Conference on Physics and Metallurgy of Superconductors (the same series as the Consultants Bureau translation (B)). The conference took place in 1968, but some papers appear to have been subsequently revised. The editor (E. M. Savitskii) points out as evidence of the "deepening" of research work in this area the beginning of the use of electronic specific heat and X-ray investigations to connect electronic structure and superconducting properties, and commencement of studies on single-crystal superconducting materials. This Soviet work is clearly at least 3 or 4 years out of date in comparison with Western work.

(D) purports to contain papers from a 1969 conference on applications of low temperatures, but some of the references are newer than that. Of 14 short articles, one is on refrigeration, one on aluminum coils, and the rest on superconducting devices (dc and ac machines, solenoids, cables, transformers). The contributors are all from the National Research Institute of Electrical Machine Construction, Leningrad. They have more than 40 superconducting solenoids or magnets in operation there, but apparently none above 5T*. Working models of motors and generators are mentioned and described briefly, but there is not too much said about the superconducting materials used. One article on flux-pump machines is strictly a review of Western work.

The short book (E) by Ivanov and coworkers (of the A. A. Baikov Metallurgical Institute, Moscow) appears to be a thorough review of both Soviet and non-Soviet work on the phases, gross superconducting properties (T_c, H_c, J_c), and mechanical properties of these alloys. In the binary alloys, the Soviets appear to have mainly followed Western work. In the ternaries, Japanese and Soviet work has predominated, particularly on the Ti-Zr-Nb system, while the Soviets have done the bulk of the work on the quaternaries, including all of the related superconducting work (by the book's authors, some not presented elsewhere) up to that time. Some of the work on ternary and quaternary alloys with hafnium is also discussed in two articles in Physics of Metals and Metallography.[12] These conclude that adding hafnium to Nb-Zr or Nb-Ti-Zr alloys does not improve superconducting properties.

The volume (F) has a couple of authors in common with (D), and may emanate from the same institute. It is rather disappointing, since it describes almost no actual work going on in the USSR at all, and few applications elsewhere of superconductivity in

*T = Tesla = Webers/m^2

specifically marine situations. It rather looks like a less-than-successful effort to justify research efforts in terms of practical applications. The devices described are almost without exception non-Soviet ones. There is a short description of a Soviet MHD generator using a superconducting magnet and an account of an experimental flux pump generator. There are a few other Soviet books on superconducting materials and applications, but they were not available to us.

ANALYSIS OF SPECIFIC RESEARCH AREAS

Superconducting Electrical Machinery in the USSR

Serious thinking about development of cryogenic electrical machines appears to have begun in the USSR almost with the discovery of hard superconductors. A considerable amount of conceptual design work has been done, and several experimental machines are known to have been constructed or to be under construction. Unipolar, commutative-dc and single-phase and polyphase ac machines have been considered--unipolar machines to a greater extent than in the US. There has also been much work on magnetohydrodynamic generators using superconducting magnets, but this will not be reviewed here. Extensive design studies, and possibly some experimental results,[6,13] have gradually led Soviet investigators to the belief that at least in the high-power (10 megawatt) range, synchronous ac generators are superior to unipolar generators and to other types of generators and the bulk of the generator work now appears to be aimed at ac. Using superconducting field coils yields a much larger relative improvement in power output per unit weight in the case of a unipolar machine, but the ultimate calculated lower power limit for this type of device can easily be exceeded by using superconducting coils in a synchronous machine. Fixed-field designs were the first to be considered and they appear to be still in contention with rotating-field arrangements.

One of the first Soviet test machines to be described[14] was a dc machine using a 20,000 Oersted Nb_3Sn magnet. A hypothetical rotating-superconducting-disk ac machine[15] of 1966 used pure niobium (apparently an adaptation of a Western idea). The same article discusses a design for a 600 MW, 3600 rpm generator using a fixed 10T Nb_3Sn magnet. A dc motor with a niobium cylinder rotor and superconducting excitation coils of Nb-Zr-Ti alloy wire (composition unspecified) was described[16] in 1969. This machine was built and tested at Kharkov Military Engineering

College. It reached 1500 rpm in liquid helium with an output torque of 35×10^{-4} N·m(34×10^{-4} ft-lb) and drew 22.5 watts. The same experimenter built a rather similar ac motor.[17] Comparative design work carried out[6,13] at the Leningrad Electrical Machinery Construction Institute assumed fixed Nb_3Sn magnets of up to 5T strength. A model 2.7 kw dc generator was built and tested using 65BT alloy wire* for the field coils. At the same institute there was under construction around 1969 a 200 kw synchronous generator with fixed interior field coils of 1920 turns of 8-strand cable of SS-2 wire producing a transverse field of 6T. A newspaper article[18] apparently describing a similar machine says the coils are of a Nb-Ti alloy. (The design may be somewhat similar to the Westinghouse 5 MW design[19]). A 3-phase 10 kw generator which has been tested at I. V. Kurchatov Atomic Energy Institute, Moscow, has 2 fixed solenoids of unspecified material producing 2.5T between them. For other power uses, such as an experimental inductive store[20], transformers, and cables[6], 65BT alloy wire seems to be the preferred material.

To summarize, pure niobium, Nb_3Sn, and various ductile niobium alloys have been used in Soviet electrical machinery. There does not seem to be much Soviet work on pure niobium. There is a great deal of work in the areas of Nb_3Sn and other materials with the A15 structure and on the ductile alloys.

Cladding

Superconducting wires must be sheathed with or embedded in a good normal conductor in order to provide a low resistance path in case some of the wire should suddenly go normal. Sheathing is also important in preventing flux-jump instabilities.[21] The theory of Wilson, et al.[22] shows that the use of a high-conductivity matrix allows the use of thicker wires; however a multifilament cable must be helically twisted more tightly if it is to be clad in a high-conductivity matrix, so some tradeoff is presumably necessary. Copper seems to be preferred as a cladding material in both the US and the USSR, while a copper-nickel alloy is preferred in the UK[9] and aluminum in France and Japan[23]. The Japanese authors claim a rather impressive list of advantages for aluminum. There does not seem to have been much systematic study of cladding in the USSR until recently. Perhaps most of their

*Some Soviet superconducting alloy designations are explained in Table 1.

TABLE 1. SOME SOVIET SUPERCONDUCTING WIRE ALLOYS

Designation	Composition, at % Nb	Ti	Zr	Other	Comments
SS-2	50	25	25		Widely used since around 1967
60T	40	60			T-60, also referred to, is probably same
35BT	30	60-65	5-10		Some guesswork on Ti-Zr composition
65BT	65	25	8.5-9	1-1.5[a]	
NTS-30	70		30		
NTS-50	50		50		
NT-1	25	75			Used in bulk for magnetic shielding (NT may also refer to Nb-Ta alloys)
RNS-2	----------unknown----------				A wire, possibly Nb-Zr with cladding, which has been used in a 0.4T magnet
Patent 287310 (Savitskii et al.)	40-60		bal.	Sn 0.5-2	Sn supposed to increase J_c, improve cold-working properties
Patent 298825 (Savitskii et al.)	bal.	40-50		Cu 3-8	Cu supposed to increase J_c, lower cost
KSMI-6	-----cable designation-----				Cable of 6 strands Cu-plated 65BT, 1 strand In-impregnated Cu.

(a) unspecified

wires worked well enough most of the time. In the last 2 or 3 years, some studies of cladding have begun to appear. These range from straightforward investigation of the effects of thickness and adherence of copper coatings on the temperature dependence of the critical current in copper wires[24] to fairly significant correction[25] of Stekly's theory[26] of current flow in composite conductors. This correction, (which is simply that the current in the superconductor in the "resistive" state can exceed the usual critical current because of the voltage drop in the superconductor maintained by the parallel drop in the cladding) can amount to 10-15% and appears to be well verified by measurements[27] on Nb-Ti alloy 7-strand cables. There is also some work reported[28] on forming V_3Ga ribbon with a copper (eventually a Cu-Ga) coating. This work, which was undertaken to increase the speed of formation of the V_3Ga as well as to provide a low-resistance path, is based on earlier Japanese research. Successful cables of V_3Ga on vanadium had been demonstrated earlier.[29] V_3Ga tape has only recently become available in the US, from Intermagnetics General Corp., Guilderland, N.Y.. It is difficult to compare these investigations with current US work because of the strong likelihood that any good new US cladding ideas are being held proprietary. In the USSR, Sychev and Al'tov have been working on these problems for at least 5 years and appear to be making progress.

Materials with A15 Structures

While it is unlikely that anyone would try to use Nb_3Sn or the other very brittle materials with the A15 structure in the rotating parts of electrical machines, these materials are being used in stationary parts. Designs are still being pursued in the USSR involving fixed superconducting coils, which, if not subjected to too much vibration, could be made of Nb_3Sn, and the characteristics of that material are adopted in designs for very large machines. Such materials might also be used in superconducting bearings of electrical machines and elsewhere and are also of interest because of the high T_c's and H_c's which have been attained in them. There is also a slight chance that more ductile materials of similar structure might be found.

Severe difficulties appear to have been encountered in the USSR in producing flexible Nb_3Sn ribbon in quantity, although some Nb_3Sn produced by diffusion[30] on a Nb strip was available as early as 1961. A 12 centimeter inside diameter,

30,000 Oersted Nb_3Sn-ribbon solenoid built as late as 1970 at Dubna[31] was considered "experimental", and a general discussion[32] probably written in early 1970 described four Western methods of producing flexible Nb_3Sn ribbon and no Soviet ones. Arkharov and coworkers[33] in 1965 or 1966 described a method of depositing 1 to 6 μm of Nb_3Sn on a moving platinum or 80Ni-20Cr wire from chloride ($NbCl_5$ and $SnCl_4$) vapors. The use of $SnCl_4$ and a low reaction temperature, preventing the formation of $NbCl_3$, is an advance over Hanck's methods. (A good short discussion of Western preparation methods is given by Echarri and Spadoni[34].) In 1968 the same experiment was described again,[35] only with the additional information that tantalum made an unsuitable substrate. It appears that superconducting magnets of Nb_3Sn for research work have been very difficult to obtain in the USSR, although this is a difficult point to document fully. Finally in 1969 and 1970 claims of Soviet success in producing Nb_3Sn in usable forms began to appear. A method (apparently then not beyond the experimental stage in the USSR) of obtaining this material by drawing niobium ribbon through liquid tin is described in Reference [5] (p 124). Good critical current densities, 10^5 A/cm^2 were obtained in some instances. Apparently more successful than this was the work of Kunakov et al.[36], who after a study of the regions of stability of the intermetallic compounds of the Nb-Sn system (confirming earlier Western work) succeeded in making wires, cables, and tapes by the solid-state diffusion method. The cable, which is formed into the shape of ultimate use (somewhat as in Kunzler's original method[37]) before the 10 μm Nb_3Sn layer is created on 70 μm niobium filaments, had a critical current of only 10^4 A/cm^2 in a 6T field, but this appears to have been predominately a contacting problem. The flexible Nb_3Sn tape, 6.25 mm wide, produced by Kunakov's group appears to have a critical current around 10^5 A/cm^2, comparable with Western materials.

It is evident that different research groups in the USSR were assigned to reproduce and perhaps to improve on the various methods of producing "useful" Nb_3Sn that had been developed elsewhere. It is not clear why they met with difficulties, since unsuccessful work seldom gets published, but the problems seem to have been overcome, and Nb_3Sn produced by several methods is now available in the USSR, although the quantity being produced is not known. Thus while the Soviets were 4 or 5 years behind at one time, there have been no outstanding US improvements for several years, and the USSR is close to catching up. The general unavailability of high-field magnets (of 10 T and over, say) probably has

hampered other Soviet research on type-II superconductors, to say nothing of its effect on work in other fields.

More fundamental studies of Nb_3Sn and related compounds began in the USSR at about the same time as the work on production of wires and ribbons. These efforts met with a degree of success in the discovery of the high transition temperatures of $Nb_3Al_{1-x}Ge_x$ solid solutions.[38] Interest in these materials has continued strong since that time. The bulk of the work is being done by part of Alekseevski's group at the Vavilov Institute for Physical Problems, Moscow, and by V. M. Pan and coworkers at the Institute for Metal Physics of the Ukranian Academy of Sciences, Kiev. Research on these materials is also being done at S. M. Kirov Urals Polytechnic Institute, and in several other laboratories.

A good part of the Soviet work on these materials during the 1960's was devoted to determining the phase diagrams of the binary and then pseudobinary systems based both on niobium and on vanadium, with the objectives of learning how to prepare single-phase stoichiometric material and of determining the effect on the transition temperature of departures from stoichiometry. These worthy motives seem to have produced a net deleterious effect, though, since many of the phase diagrams worked out at that time turned out to be wrong in some significant aspects. In particular, it was generally agreed by Soviet workers that the region of stability of the β-W phase in Nb_3Sn extended to room temperature,[4] although the width in composition of the stable region was the subject of debate. Correcting this impression helped Kunakov et al.[36] to develop the Nb_3Sn wire mentioned above. In Nb_3Ga, on the other hand, Myzenkova et al.[39] apparently found no stable β-W region at low temperature, in contrast to what has been determined recently in the US.[40] Thus one might say they were not in a good position to find the curve in the phase boundary and the method of making Nb_3Ga with a transition[40,41] above 20K, but of course no one was really "in a position" to do this rather tricky work until it was actually done. There does not seem to be any work on this compound at present in the USSR, but this situation may be expected to change as the Soviets respond to US developments. Vapor-deposited Nb_3Ga tape is now available commercially in the US from Columbia Superconductor and Cryogenics Company, Allentown, Pa.

Other recent Soviet work worth mentioning is concerned with deformation of Nb_3Sn, with vanadium-based binaries and ternaries, and with other Nb_3Al-based materials. The work on deformation is under the direction of L. F. Vereshchagin at the Institute of High-Pressure Physics, Akademgorodok. By hydroextrusion, deformations of pure Nb_3Sn rods (1.5 to 30 mm diameter) of up to 65 percent can be achieved. The changes in composition[42] and T_c[43] on such deformation have been measured. The A15 lattice becomes niobium-rich on deformation, and it is suggested that $NbSn_2$ forms in compensation. The transition temperature drops to about 12K, but can be restored by annealing at 900 C. The Soviet investigators don't know whether this phenomenon is caused by stress removal or by composition change. While the process of deformation is far ahead of anything done in the US on this sort of material, one has the impression that the authors are still just playing around with the apparatus; for serious work they should be doing electron microscopy on their samples.

A15 compounds based on vanadium are of interest because of the possibility that they may have higher T_c's than niobium-based ones, primarily because of their higher Debye temperatures.[44] Ternary compounds, including $(V_{1-x}Cr_x)_3Si$, $V_3Al_{1-x}Ge_x$, and $V_3Ga_{1-x}Ge_x$ are being investigated at Urals Polytechnic Institute.[45] In the V_3(Al-Ge) system, the maximum T_c so far obtained is about 12.5K for $V_3Al_{.25}Ge_{.75}$ (the other way around in Al/Ge ratio from the corresponding niobium-based material). This research group appears to have a wide variety of facilities for preparation and study of these materials. Besides their work on the vanadium compounds, they have prepared $Nb_3Al_{.75}Ge_{.25}$ with T_c of 20.3K (see below) and Kodess et al., of that group, have found X-ray and NMR (nuclear magnetic resonance) evidence of the martensitic transformation[45] in this material. The Urals Polytechnic group seems to be the only one in the USSR with a serious interest in this transformation, which has been the principal focus of US work on the A15 materials for the last several years (that is, attempting to determine whether it has any significance for or relation to the superconducting properties has been the focus). A number of alloys based on V_3Ga were prepared at Kiev.[46] In addition to the expected appearance of the β-W phase when niobium or elements of the IIIB, or IVB groups are added to the V-Ga binary, this phase alone was found in as-cast specimens containing 5 percent manganese, chromium, technetium, platinium, rhodium, or iridium. These additives all have a deleterious effect on T_c; however platinum and tin in particular, increase the $\beta \rightarrow \alpha$ conversion temperature substantially.

There is a question, of course, as to whether finely dispersed α-phase (bcc solid solution) particles may not increase the critical current density. Pan and coworkers also found that by making V_3Ga-based ternaries vanadium-rich to the point that the V_3Ga was dispersed in the α-phase solid solution, a deformable alloy with good superconducting properties could be obtained.[47] The transition is diffuse, occurring from 11.5 to 15K. They do not seem to have followed up this work, though, nor similar work with Nb_3Al,[48] so perhaps the expected results proved chimerical. These alloys show high critical currents of densities (over 5×10^4 A/cm^2 measured in a 12,000 Oersted field, and over 3×10^5 A/cm^2 extrapolated a little optimistically to zero field). However they also found that the maximum T_c and the sharpest transition was achieved for aluminum-rich compositions[49] presumably because the stoichiometry of the β-W phase was maintained.

As one might expect, the greatest amount of work on the $Nb_3Al_{1-x}Ge_x$ system is being done by Alekseevskii's group (discoverer of the high transition temperatures of this system), although the system is also under investigation several other places. We mentioned above the work at Urals Polytechnic Institute. Workers at the Central Ferrous Metallurgy Research Institute, Moscow, studied the ternary phase diagram[50], and showed that the high T_c region has a rather complicated shape (probably representing a net result of conflicting tendencies), although they were not able to produce material of high transition temperature. Pan has studied the related $Nb_3Al_{1-x}Si_x$ system[51], finding only a slight improvement (0.5K) in T_c so far, and his group has done interesting positron annihilation and elastic constant work[52]. Pan's group interpreted the elastic constant results on the basis of strong-coupling theory,[44] which seems to have been rather slow to catch on in the USSR. They justify using this theory rather than the somewhat simpler Labbé-Friedel(L-F) model on the basis that there is no martensitic transformation in this material, apparently not having heard of the results of Kodess et al.[45] discussed above. (Better reasons for rejecting the L-F model are given by Rehwald et al.[53]) In reference [52], the authors come to the conclusion that the increase in T_c is a result primarily of increased electron-phonon (e-p) coupling rather than a more strongly screened coulomb interaction. (Ordering in the Al-Ge sublattice would be one way to produce the increased e-p coupling.) However this result has to be taken with a grain of salt, since the band picture adopted is very over-simplified. Alekseevskii seems to have been systematically studying all the properties of the

$Nb_3Al_{1-x}Ge_x$ system, including recent work on Knight shift[54] and susceptibility[55] which he interprets to support his favorite hypothesis, that of ordering in the Al-Ge sublattice, for which some x-ray evidence[56] had been presented earlier. (According to earlier ideas of Matthias, it is only the niobium-versus-everything-else stoichiometry which is important for obtaining a high T_c.) It is interesting to note that the highest transition temperature shown in these experiments is 20.3K (both by Alekseevskii and by the Urals group; Pan gets 20.1K), as compared with a somewhat dubious world record[1,57] of 20.75K.

The above discussion should serve to show that A15 compounds are being extensively studied in the USSR, and that good quality work is being done. They could do a little better on theoretical interpretation (the well-known Soviet disdain for band theory may hurt them some here) and they need to pay more attention to crystal growth, neutron diffraction, and microstructure in their development of superconductive materials. They have not been careful in impurity analysis in superconductors in the past, but have the capability and interest to do a good job now. As late as 1971, a Soviet paper[58] was published on development of vacuum-fusion determination of oxygen in various A15's. It is somewhat surprising that no work on increasing J_c in the ternaries was reported, as the ternaries are not going to be useful unless this is done.[1] Still, given what appears to be the declining state of US work in the field (and a suspicion that many of the US investigators are more interested in soft modes and phase-transition theory than in high Tc's) we would expect that if there are to be other superconductors with A15 structure of T_c > 20K, and if it is just between the US and the USSR, the Soviets are more likely to find them.

Ductile Niobium Alloys

Soviet research on Nb-Zr alloys for producing high magnetic fields began early in 1962[59], not long after the discovery of high-field superconductivity in these materials. Already in 1961 a 20,000 Oersted superconducting magnet of pure niobium had been built.[60] By 1965, studies of a variety of niobium alloys were underway,[4] and considerable work is still being done on them. Besides studies of phase diagrams (which featured the usual disagreements, some persisting nearly to the present day[61]), typical research of the period involved attempts to assess the influence of various mechanical and thermal treatments on J_c (and to a lesser extent on H_c and T_c) and to relate this to the more obvious changes in the material structure. Most of this work dealt with only a few samples and the results of only a few

treatments were described; it is very difficult to come to definite conclusions as to what was accomplished, particularly with hindsight as to the complexity of many of the metallurgical problems involved. Fortunately many of the results are summarized in reference [7]. We recall at this point that the authors of this book made extensive studies of the ternaries[62] and quaternaries[7,12] containing up to 56 at % hafnium, and concluded that hafnium generally had a deleterious effect on T_c, H_c, and J_c. Nb-Hf alloys are of some interest for studies of flux pinning because of the relatively simple way in which precipitates form[63], but nonetheless we shall not discuss hafnium alloys further, and in fact will discuss only the Nb-Ti-Zr systems on which all commercial wires are based.

Apparently it was decided rather early in the USSR to select a few compositions in the ductile niobium systems for wire development, starting with Nb-Zr for coils with fields up to about 5T. When it came time to think about developing higher H_c wires, ternaries were selected over Nb-Ti alloys, possibly following work of Doi[64] in Japan, perhaps on the basis of a single report[65] that high H_c's fell in a region of low J_c's in the Nb-Ti system, although it was recognized early on that Nb-Ti alloys were much more satisfactory than Nb-Zr from the standpoint of not having their properties degraded upon forming the wire into coils.[65] Now Nb-Ti alloys are coming into wider use, as mentioned earlier, although ternaries are still prominent. Some designations and compositions for common Soviet superconducting wire alloys (and some not so common) are given in Table 1. It is not clear whether in the various cases these designations refer to the bare wire, to the wire plus copper, or to the wire plus copper plus insulation, nor whether the designation requires a specific wire diameter. These wires seem to have worked well enough, but little was done originally on their basic characteristics, and over the past 5 years various research groups in the USSR have found themselves in the slightly anomalous position of doing on these more-or-less "commercially" available products the fundamental research work which, they may well feel, should have played a role in selection of the most desirable materials and the best manufacturing processes for these wires. It seems clear from the amount of research going on that the Soviets believe that worthwhile advances can be made in these materials.

The research groups most heavily involved in ductile niobium alloy work at present are located at the Physicotechnical Institute for Low Temperatures of the Ukrainian Academy of Sciences, Kharkov; at the Baikov Institute of Metallurgy, Moscow; the

Bardin Central Ferrous Metallurgy Research Institute, Moscow; and at the Lebedev Physics Institute and the Institute for Metal Physics of the USSR Academy of Sciences, Moscow.

Areas of considerable present research interest include the following:

(1) Factors affecting properties, particularly J_c, of commercial wires and alloy materials,

(2) Effects of cold working, particularly cold-drawing into wire, on J_c and other properties,

(3) Effects of ω-phase precipitate on flux pinning and other properties, particularly in $Nb_{.78}Ti_{.22}$, and

(4) Relationships among electronic and superconducting properties in these materials.

There is considerable overlap among these items.

Work on more-or-less standard-alloy wires and materials includes straightforward studies of effects of wire diameter and configuration on apparent J_c through effects on heat transfer to liquid helium[66], and investigation of properties of cold-deformed and tempered 65BT[67], 35BT[68] and other ternary alloys[69]. The interpretation of the results of the latter investigations are made more tenuous by the circumstance that in no case was it possible unequivocally to identify by electron diffraction the new phase which precipated on short-time aging at moderate temperatures (around 300-400 C). This phase doubtless is the hexagonal metastable ω phase (see below) which is of importance in obtaining high J_c in Nb-Ti alloys. Zirconium, in the relatively small amounts used, does not enter the precipitate. At higher annealing temperatures, α (hcp-titanium) phase precipitates; in 65BT, which has a much lower titanium content, only the α phase may occur. Buynov et al. pointed out[67] that the growth of the alpha precipitate leads eventually to formation of dislocation loops.

Among more unusual work on the standard alloys are direct observations of the flux lattice,[70] though not in large fields, and field-ion-microscope observations[71] on cold-worked annealed 60T alloy. The authors of the latter reference claim that these indicated a network of very niobium-rich filaments or plates, which are held to be responsible for the high J_c's, in confirmation of a long-held view of Lazarev's[72]. In view of the difficulty of the technique and the disagreement with results of other methods, one is perhaps justified in being somewhat skeptical. There is some evidence of niobium-rich shells found

around ω-phase precipitates.[73] It will be helpful to recall at this point a few of the properties of the ω phase already alluded to. This hexagonal titanium-rich phase precipitates out as a metastable form when β-(bcc-niobium) phase alloys are annealed at temperatures around 400 C for not too long a time. The precipitates thus found are extremely fine, difficult to discern by x-ray diffraction, and it is believed that when they are of an appropriate size and spacing they may serve as effective flux pinning sites and thus be primarily responsible for the high J_c's. (There are other metastable phases in this system but we shall not discuss them here.) Near the equilibrium $\beta \rightarrow \alpha + \beta$ phase boundary[74], and in particular for $Ti_{.78}Nb_{.22}$ aged near 400 C, one may obtain by appropriate heat treatment the following states:[75]

(1) β (bcc) - phase solid solution,

(2) β-phase plus ω-phase precipitates of composition $\sim Ti_{.83}Nb_{.17}$.

(3) β-phase plus α-phase precipitates of composition $\sim Ti_{.95}Nb_{.05}$.

The $Ti_{.78}Nb_{.22}$ composition has been extensively studied over the past few years by Karasik and coworkers at the Lebedev Physics Institute.[76] They have investigated critical current and magnetization in both transverse ($\vec{H} \perp \vec{J}$) and longitudinal[77] ($\vec{H} \parallel \vec{J}$) applied fields for a large number of samples of known microstructure. "Peak effects" (the presence of a subsidiary maximum in the J_c (H) curve away from H=0) observed in a number of samples are explained in terms of a model of driving fairly small (90 x 560 angstroms) ω-phase particles normal in the applied field, thereby increasing their ability to stabilize the transport current by rigidly pinning the fluxon lattice. The critical current for "non-peak" samples calculated on the basis of rigid pinning is close to experimental values. This is <u>not</u> one of the mechanisms for the peak effect discussed by Dew-Hughes.[1] For smaller ω-phase particles, the inclusions are driven into the superconducting state at temperatures above their bulk T_c by the proximity effect if the coherence length is large enough. This was demonstrated by magnetization measurements. When $\vec{H}$ is parallel to $\vec{J}$, a sharp dip followed by a high peak occurs in non-coldworked samples, a phenomenon earlier observed by Sekula et al.[78] in other alloys, and explained in the present paper (reference[77]) along the lines they suggested. Karasik et al. argue that measurements of the longitudinal critical current density are useful for determining the ultimate critical current density obtainable in the material. $Ti_{.75}Nb_{.25}$ and $Ti_{.66}Nb_{.34}$ alloys have also recently been studied rather extensively.[79] A recent paper[80] on several Nb-Ti alloys indicates that J_c can be increased by ω-phase precipitation, as was already pointed out by Bychkov et al.[76] This recent work does not appear so careful or thorough as

other Soviet studies in this research area. An unusual material about which there is a great deal in the Soviet literature[79], but none we have come across in Western references, is $Zr_{.96}Nb_{.04}$. When properly tempered, this alloy is claimed to have a precipitate of almost pure niobium threads, which can be superconducting even though the matrix is normal, thus leading to behavior somewhat like that of "artificial" filamentary superconductors made by impregnating porous glass with metal. Possibly similar are the niobium-(more likely NbN-, we think) filament-in-copper superconductors announced by Tsuei.[81]

Recent work on electronic properties of superconducting niobium alloys includes studies of specific heat[82], thermal conductivity[83], optical properties[84], and Mossbauer effect.[85] The thermal properties are interpreted in terms of a two-gap model. The Mossbauer work is said to demonstrate a relation between chemical shift of the lines and critical current density which is related to presumed microstructure changes.

It is clear that there is (or was a couple of years ago--most of the available references pertain to work one or two years old) a good deal of Soviet work on ductile niobium alloys, some of it comparable in quality with the British, West German, and US work of the time. There seems to be rather little work in this area in the US at present--some work at Westinghouse, possibly still some at Oak Ridge, a little related work at Battelle, and probably considerable proprietary work of which we are unaware. One would say that the USSR is somewhat ahead of the US, at least in experimental effort on ductile niobium alloys, but we believe that there is intensive work still underway in the UK and West Germany (see references [1] and [2], for instance), and both the US and the USSR may merely keep abreast of these developments. There is also a question to be faced of whether present ductile niobium alloys may already by good enough, and whether possible J_c increases are likely enough and large enough to justify much additional research.

High T_c Materials

Attempts at increasing T_c can be divided into

(1) Improvements in "standard" materials,

(2) Development of novel mechanisms.

The second category could be further divided into

(2a) Using phonon coupling

(2b) Using exciton coupling.

There is a lot of overlap among these categories[86] and room for speculation as to what may go on in particular cases as well. The "standard" materials have been discussed above (at least the A15's have been, and we are not going to discuss the nitrides and carbides, which are perhaps outside contenders). Here we just give a list (Table 2) of the possible mechanisms for achieving high T_c and a rather subjective impression of relative efforts without much attempt at full documentation.

Just a few points deserve comment. The first high-pressure-formed high-T_c superconductors, such as Bi III, were found in the USSR. The principal work on pressure synthesis in the US is by Giorgi and coworkers at Los Alamos.[88] They found the remarkable high-pressure-stabilized material $Th_{.3}Y_{.7}C_{1.55}$, with a bcc Pu_2C_3 type of structure and a T_c of 17K, by far the highest ever achieved by this technique. The Soviet work on sandwich-like materials is being done by some of Alekseevskii's group.[89] The motivation behind their choice of materials seems weak and we get the impression that they don't really have their hearts in this work. The enthusiasm of Bardeen[86] for excitonic coupling using metal-semiconductor sandwiches will no doubt lead to increased effort on these structures everywhere. While the US seems to have overtaken a slight Soviet lead in high-pressure synthesis of superconductors, there is great effort in the USSR toward producing metallic hydrogen, and in fact a recent claim[90] that it has been made. If metallic hydrogen turns out to be superconducting at a high temperature,* the Soviets are going to find it out first, because of their strong lead in development of very-high-pressure apparatus.

PROGNOSIS

As we have seen, Soviet activity in many areas of the field of superconducting materials of practical importance is high. There is no reason to expect that they will not continue to improve the instrumentation necessary for the characterization and study of these materials. There are no serious theoretical problems impeding development, although there is much about "technical" superconducting materials that is not understood in detail. At the same time, US interest in these areas appears to be declining. Thus, unless some potentially useful novel high T_c material is developed in the US, all that is required for the USSR to take a definite lead in

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*The reason for supposing this might be so is just that the Debye temperature should be very high in metallic hydrogen because its ionic mass is small. The best simple discussion of this is a popular article by Khalatnikov.[91]

TABLE 2. RELATIVE US AND SOVIET EFFORTS ON PROPOSED CLASSES OF MATERIALS FOR HIGH T_c SUPERCONDUCTORS

Type of Material	Level of effort	
	USSR	US
(1) Improved conventional	Strong	Moderate, decreasing
(2) High-pressure synthesized metastable forms	Strong[87]	Not too large, but effective[88]
(3) Intercalation and layered compounds	Some, little published[92]	Intensive[93]
(4) One-dimensional conductors other than Little polymers	One group, at least[94]	Some published, growing rapidly[95,96]
(5) Granular materials	No recent work known	Was work at Corning[97], may still be some
(6) Thin films	No recent work known	Moribund
(7) Metal-semiconductor (or -dielectric) sandwiches	A little work in 1 group[89]	At least 1 group, will increase[86]
(8) Metallic hydrogen	Strong[90]	Moderate
(9) Side-chain polymers of Little type	No recent work found	Little, a few others, probably still plugging away
(10) Biological materials	No recent work found	Some effort, probably of low potential

the field of superconducting materials within five years is to keep going at their present rate. Barring complete cessation of US effort, the Soviets could not obtain a large lead in any event, perhaps a year at most. Of course a lot of good work is going on elsewhere, particularly in Japan, Great Britain, and West Germany, and the results of this work is bound to affect what happens in both the US and the USSR. In the field of novel-mechanism superconductors, one can do no better than to quote Anderson:[98] "--the only safe prediction is that conventional extrapolations of any type--including what types of materials to look for or what 'superconductivity' itself may mean--are completely unsafe."

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STAINLESS STEELS AND NON-FERROUS ALLOYS FOR CRYOGENIC EQUIPMENT RELATED TO THE USE OF SUPERCONDUCTORS

R. J. Nekervis

INTRODUCTION

Superconduction, the disappearance of electrical resistance in metals and alloys, was discovered in 1911. For nearly 50 years it remained an object mainly of academic interest. With the discovery in 1960 of alloys that retain their zero resistance even under high current densities and in strong magnetic fields, it has become potentially the most important industrial application of the technology of very low temperatures, that is, those attainable in liquid helium environments.

Superconduction in metals and alloys is an ordering phenomenon that in many ways is akin to another ordering phenomenon that occurs in helium itself; when liquid helium is cooled under its vapor, it does not solidify. At a well defined temperature, ordering sets in, producing the so-called helium II modification or superfluid helium, which has several unusual properties, among them vanishing viscosity, and a several millionfold increase in thermal conductivity. As a result of the discovery of these properties, research in the field of cryogenics, particularly that related to superconducting machinery, has been stepped up since the early 1960s.

CONCLUSIONS

1. The patterns of development of constructional metals and alloys for cryogenic application in superconducting electrical machinery in the US and USSR are very similar.

2. High-yield low-carbon austenitic, nitrogen-modified, standard grade stainless steels have been developed by both the US and USSR for cryogenic applications. Properties of the equivalent US- and Soviet-developed grades are essentially the same.

3. The Soviets have systematically developed chromium-nickel-manganese-nitrogen containing stainless steels; one of these, 21-16-6-N, exhibits the best combination of high tensile strength with the lowest loss of impact strength and ductility in the range, +20 to -269 C (4 K) of any of the stable austenitic stainless steels tested to date. The Soviets have a temporary lead over the US in the application of steels of this type; the US has such steels but this particular composition does not appear to have been tried in cryogenic equipment for superconducting electrical machinery.

4. The Soviets appear to be first to specify a titanium alloy for use as a rotor material for a high powered turbogenerator with superconducting windings; the alloy specified AT2-2, a Ti-2.5 percent Zr-1.3 percent Mo alpha-titanium alloy has no US equivalent. It appears to fulfill the specific requirements of good electrical conductivity at low temperatures, absence of temper brittleness, complete absence of magnetization, and good weldability required for a 2000 megawatt turbogenerator design.

5. The new Soviet stainless steel alloy 21-16-6-N appears to have superceded the AT-2 titanium alloy as a candidate constructional material for superconducting electrical machinery.

BACKGROUND

Both the US and the USSR have been quite active in very low temperature research; the size of Soviet effort appears to be about equal to that of the US. Soviet laboratories are not so well equipped as US laboratories, but in spite of that the Soviets do high-quality research, demonstrating high competence on the part of their researchers. For example, they have shown considerable competence in the development and use of the helium 3-helium 4 dilution refrigerator, the best available means of attaining and maintaining ultralow temperatures, and in the development of helium liquefaction equipment.[1] They have conducted superconductivity research at very high pressures, and experimented with superconductors in space.

As was pointed out in the Introduction, in US-Soviet development of superconducting electrical machinery, Soviet researchers, along with researchers in the US, started work on the development of applications for superconductivity in electrical machinery in the early 1960s.[2,3] In short, the Soviets have been active in the development of superconducting d-c machines, a-c machines with d-c field windings, and in the application of superconducting machines on shipboard.[4-7] Concurrent development of cryogenic materials that will withstand the extremely low operating temperatures (down to 4 K) utilized in naval applications of superconducting electric machinery seems to have been accelerated in recent years.[7]

DETAILED ANALYSIS OF PRESENT STATUS

Stainless Steels as a Constructional Material for Cryogenic Equipment Related to the Use of Superconductors

The development of an intrinsically stable superconductor that, in turn, made possible the application of superconductivity in the windings of electrical machinery appears to be one of the chief factors underlying Soviet emphasis over the past few years on the performance of metallic materials down to the temperature of boiling helium, 4.2 K. Before that, the Soviets tended to limit cryogenic testing to a minimum of 20.4 K, the temperature of boiling hydrogen. In the West, where

the supply of helium was not so acute, this limitation did not apply as stringently.

In the United States, austenitic stainless steels of the AISI 300 series are the main iron-base alloys used for constructional load carrying members of cryogenic equipment. Where such equipment must operate in a magnetic field, such as superconducting electric magnets and electric machinery, non-transforming grades are specified. Probably the most widely available non-transforming stainless steel is AISI 310, which contains ~25 percent chromium and 20 percent nickel.[8] Alloys with lower nickel contents, such as AISI 316, 321 and 347, will transform to some degree at temperatures of 77 K (the boiling point of nitrogen) and below if they are deformed at these temperatures. Some grades, such as AISI 303 and 304, transform spontaneously upon cooling to these temperatures.[9] Steels with low carbon and nitrogen contents transform more readily than those with higher concentrations of these elements.[10] Also steels with a high nitrogen content show a significant increase in yield (or proof) stress; the recently developed "hi-proof" grades of 304, 316 and 347 stainless steel contain 0.2% nitrogen and have yield and tensile strengths about 15 ksi higher than those of the normal grades.

The austenitic stainless steels are weldable but they are subject to "weld decay" upon heating in the range 400-800 C (750-1560 F) if the carbon content is higher than 0.03% and carbide forming elements such as titanium or niobium are not present. Weld decay is caused by an intergranular precipitation of very thin films of chromium carbides, an effect known as "sensitization". Impact strength is impaired and, because the layer next to the chromium-carbide film is depleted in chromium, corrosion resistance also suffers.

Since a low carbon content increases the likelihood of martensitic transformation at low temperature, with its attendant disadvantages of brittleness, and dimensional and ferromagnetic changes, stabilized stainless steels such as AISI 321 and 347 are used. However, there are some drawbacks. The AISI 347 type niobium stabilized stainless steels are difficult to weld in sections larger than 3/4 inch because of the tendency toward hot cracking. Furthermore, the AISI 321 type titanium stabilized stainless steels sometimes develop titanium stringer segregation ("titanium streaking") in thin sections, causing leaks in thin-walled tubing made from it. Niobium stabilized stainless steel welding filler rods are preferred to the titanium stabilized stainless steel; titanium readily oxidizes during arc welding.

Fabrication procedures for high chromium content stainless steels are designed to avoid the formation of "sigma phase", an ordered iron-chromium structure that is formed when the steel is heated in the range 600-950 C (1110-1740 F) for long periods, and which leads to severe embrittlement at room temperature.

The main disadvantage of the widely used AISI 310 stainless steel is its relatively low tensile strength, about 30 ksi. Cold working improves it considerably but at the expense of some ductility. Higher strength stainless steel such as Armco's 21-6-9 stainless steel* which has a very stable austenitic structure at very low temperatures, has been used for load carrying members in large superconducting magnets.[8,11] The yield strength of this material at 4.2 K is around 196 ksi. Nonferrous alloys such as the nickel cobalt alloy, MP-35N** and ELI (extra-low-impurity) titanium-5 percent aluminium-2.5 percent tin alloy have also been used in the large coils of superconducting magnets; the yield strengths of these two alloys at 4.2 K are, respectively, 332 ksi and 210 ksi.[11]

Soviet utilization of stainless steels for use in superconducting electric machinery, magnets, and associated gear operating at cryogenic temperatures follows a pattern very similar to that of the US. The three most widely used Soviet grades are (1) Kh25N18 which is a near equivalent of AISI 310, (2) Kh18N10T which is the Soviet equivalent of AISI 321, and (3) Kh21N5AG7, a higher-strength, lower-nickel containing grade very similar to Armco's 21-6-9 of ductility at very low temperatures less than that of the other two Soviet grades.[12,14] Compositions of these steels are given in Table 1.

Soviet stainless steel Kh18N10T (US equivalent, AISI 321) appears to be used in cryogenic evaluation as a standard of comparison; newly developed alloys are compared with it. Also, it has been used in an experimental d-c electrical motor with superconducting winding in the manner shown in Figures 1 and 2.[4]

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* Composition, percent: 18-21.5 Cr, 5.5-7.5 Ni, 8-10 Mn, 0.15-0.40 N, 0.03 max C, 1 max Si, balance Fe

** Nominal Composition, percent: 35Ni, 35Co, 20Cr, 10Mo

TABLE 1. PRINCIPAL SOVIET WROUGHT STEELS AND ALLOYS CONSIDERED FOR CRYOGENIC EQUIPMENT RELATED TO THE USE OF SUPERCONDUCTORS

A. AUSTENITIC STAINLESS STEELS
(Percent, balance Fe)

Alloy Designation	Factory Design	Nearest US Equiv.	C	Cr	Ni	Mn	Si	Ti	N_2	P	S	Other
Kh18N10T		AISI 321	0.12 max	17/19	9/11			5x%C		0.025 max	0.025 max	
0Kh18N10T	EI 914	AISI 321	0.08 max	17/19	10/12	1/2	0.80	5x%C		0.03		
00Kh18N10T		AISI 321	0.03 max	19.4	9.20	1.3	0.41	0.35				
0Kh23N18		AISI 310	0.08	22	18.24	1.57	0.23			0.035 max	0.030 max	(may contain up to 0.10Ti)
Kh25N20		AISI 310	0.15 max	24/27	17/20	1/2	1					
21-16-6-N			0.02	20	16	6	0.4 max		0.25			Al, 0.06 max; Ca(deox). 0.1-0.15%
Kh21N5AG7	EP 222		0.07	20/22	5/6	6/8	0.70		0.15/0.25	0.030 max	0.040 max	
000Kh21N5AG7		ARMCO's 21-6-9	0.033	20.4	6.1	8	0.16		0.107	0.015	0.008	
ARMCO 21-6-9 (US)			0.03 max	18/21.5	5.5/7.5	8/10	1 max		0.15/0.40			

TABLE 1. Continued

TABLE 1. (Contd)

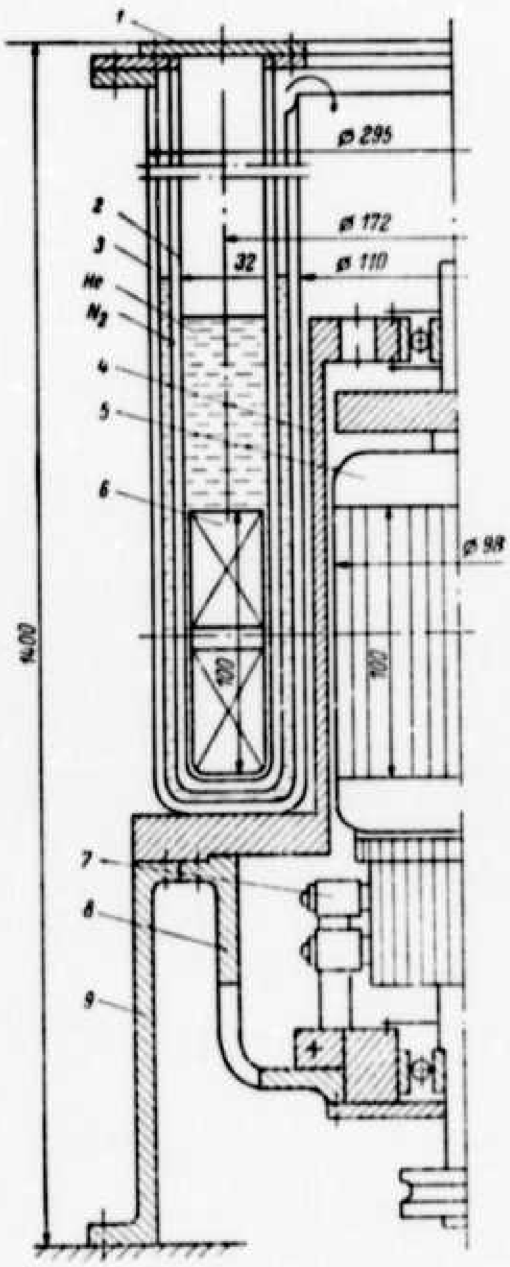
B. SOVIET TITANIUM ALLOY
(Percent, balance Ti)

Soviet Alloy Designation	Zr	Mo	Fe max	Si max	C max	N_2 max	O_2 max	H_2 max
AT2-2	2.0/3.0	0.8/1.8	0.3	0.15	0.10	0.05	0.15	0.01

C. SOVIET NICKEL BASE ALLOY
(Percent, balance Ni)

	Cr	Mo	Nb	Al	Fe	Other
KhN63MB32Yu	18	9	2.5/3.0	1.5	5	nominal composition; may contain 0.005B

(a) Low-carbon version

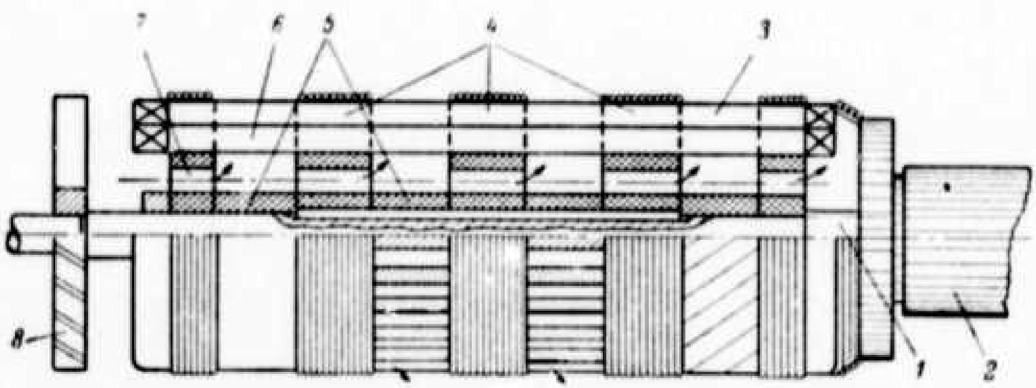


Legend

1. End plate
2. Helium vessel – made of Kh18N10T (AISI 321)
3. Nitrogen vessel – made of Kh18N10T (AISI 321)
4. Duralumin (2017) case
5. Armature (see Figure 2 for detail)
6. Coaxial coil, an indium-coated superconducting cable consisting of 3 copper-coated strands of 65BT alloy (composition, percent; Nb 65; Ti 25, Zr 8.5-9; unspecified constituents, 1-1.5), and 4 stabilizing copper strands; strand diameter, 0.27 mm
7. Bearing crosshead
8. Flange for attaching bearing assembly
9. Supports

FIGURE 1. FRONT VIEW OF A SOVIET VERTICAL D-C COMMUTATOR MOTOR WITH SUPERCONDUCTIVE BI-POLAR FIELD WINDINGS[4]

Rated at 2.7 kilowatts; dimensions are in millimeters.



Legend

1. Stainless steel shaft (composition not given)
2. Collector
3. Windings
4. Bushings
5. Bushings
6. Annular ventilation channels
7. Axial ventilation channels in bushings (4)
8. Fans

FIGURE 2. CROSS SECTION OF THE ARMATURE SHOWN IN FIGURE 1[4]

As Table 1 indicates, the Soviets have also developed low carbon, nitrogen modified steels of these and similar alloys.[15,16] Systematic development of chromium-nickel-nitrogen and chromium-nickel-manganese-nitrogen containing stainless steels showed that the combination of manganese with nitrogen was particularly effective in improving the weldability and impact strength at low temperatures.[17-24] As a consequence of these research results, the Soviets appear to favor a 21Cr-16Ni-6Mn-N_2 type of steel* for use in the range +20 to -269 C because it exhibits a combination of good tensile characteristics and a low loss of ductility and impact strength at very low temperatures (Figures 3, 4, 5, and 6).[17] A content of more than 0.08 percent residual aluminium in this steel increases the tendency toward embrittlement at low temperature; a silicon content of over 0.45 percent also has a deleterious effect.[25] Mention should be made of another Soviet chromium-manganese-nickel steel, Kh14G14N3T, which was developed as a low nickel replacement for Kh18N10T (AISI 321).[22-24] This particular grade showed an anomalous drop in strength in the temperature range -196 to -253 C, Figure 7, an indication of embrittlement according to one of the Soviet developers, D. V. Lebedev, of the Central Scientific Institute of Ferrous Metallurgy.[23]

As is the case in the US, the Soviets are conducting concurrent fatigue life studies along with developmental programs.[26-29] Machines for testing steels, aluminium, and other nonferrous metals at low temperatures under combined tension and torsion have been developed and are being used by the Soviets.[30,31] Creep has been studied at temperatures to 4.2 K and below.[32] Studies to select the most suitable brazing materials have also been reported, but unfortunately only factory designations of the best silver and copper brazing alloys were given without revealing their chemical compositions.[33] There are, of course, continuing Soviet investigations into physical properties, such as thermal and electrical conductivity, at temperatures of 4 K and below.[34,35]

In both the US and USSR, comprehensive handbooks reporting mechanical property data at low temperatures covering a wide range of metals and alloys, including steels, titanium, nickel, and aluminium, polymeric materials, composites, etc., have been published.[36-40] However, for the most part, the limiting test temperature covered in these handbooks is 20 K.

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*See Table 1 for the composition of 21-16-6-N

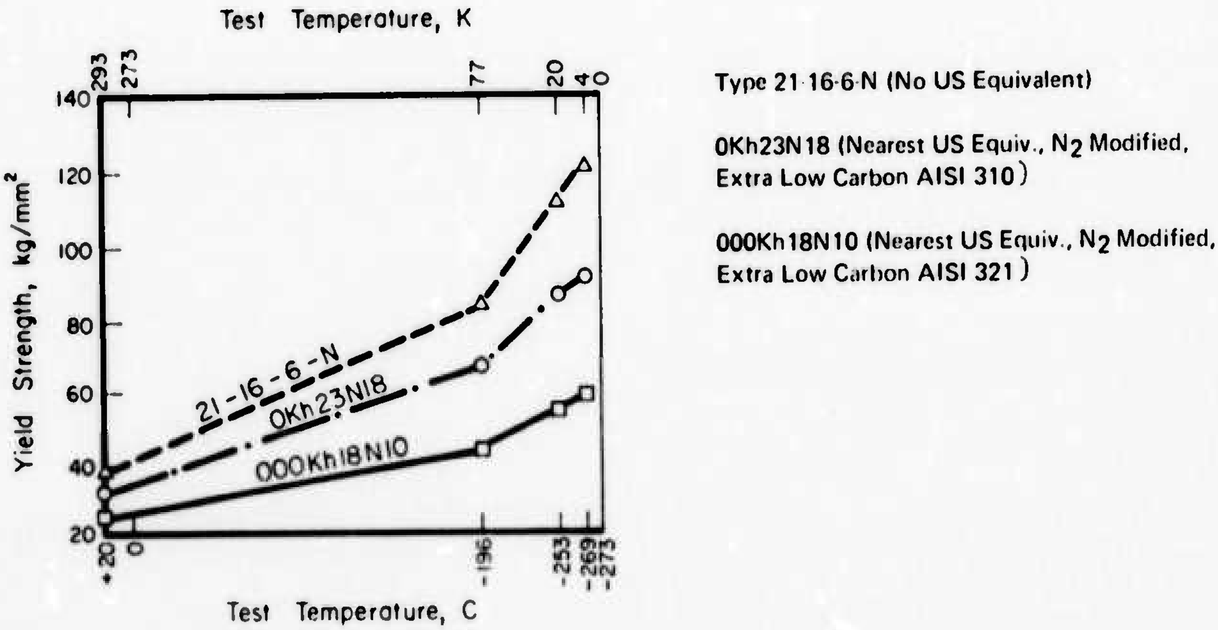


FIGURE 3. YIELD STRENGTH (0.2% OFFSET) OF SOVIET STAINLESS STEELS IN THE TEMPERATURE RANGE, +20 to -269 C[17]

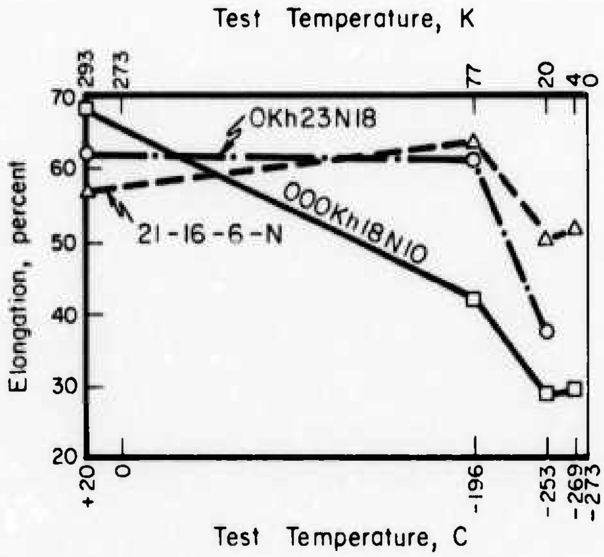


FIGURE 4. DUCTILITY OF SOVIET STAINLESS STEELS[17]

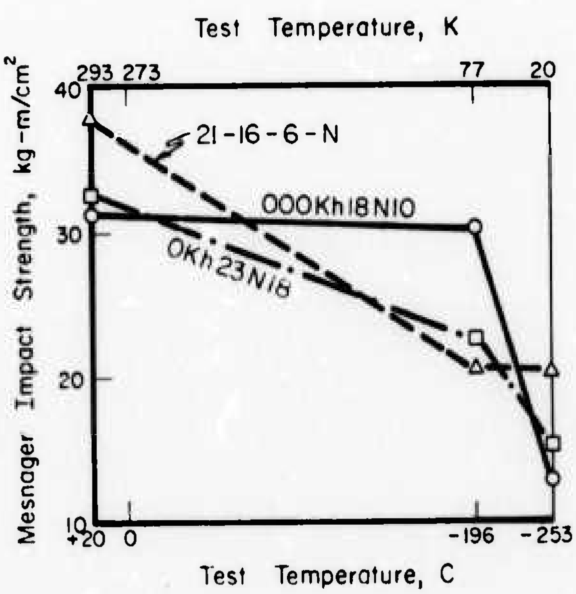


FIGURE 5. MESNAGER IMPACT STRENGTH OF SOVIET STAINLESS STEELS[17]

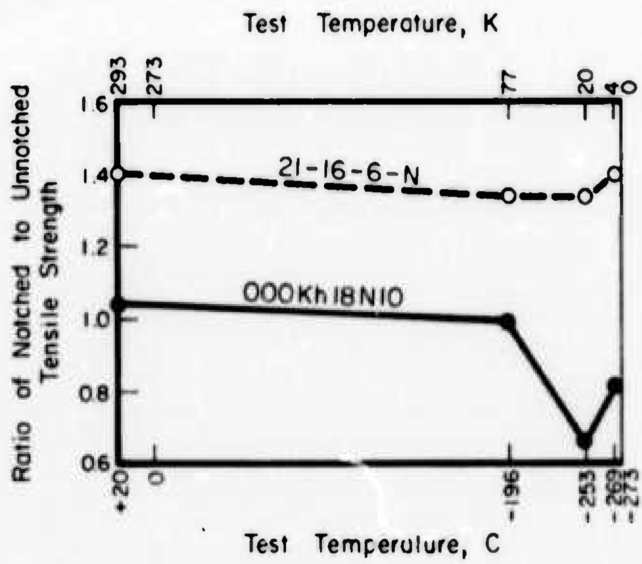


FIGURE 6. DEPENDENCE OF THE COEFFICIENT OF NOTCH SUSCEPTIBILITY ON TEMPERATURE FOR SOVIET STAINLESS STEELS[17]

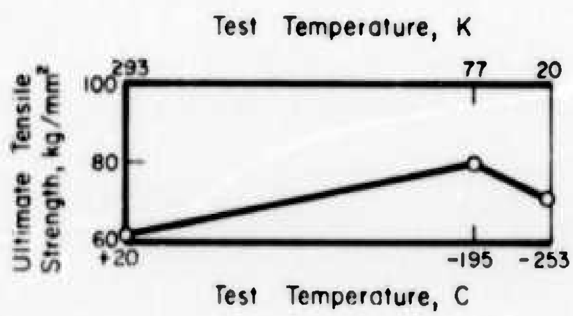


FIGURE 7. ULTIMATE TENSILE STRENGTH OF Kh14G14N3T IN THE TEMPERATURE RANGE, +20 to -253 C[23]

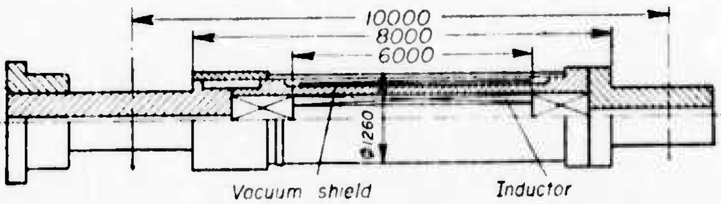
Titanium Alloys as a Constructional Material for Turbogenerator Rotors with Superconducting Windings

The Soviets have been looking into titanium alloys as a constructional material for their higher power turbogenerators with superconducting windings, those with a power of 2000 megawatts or more.[41-46] One, in particular, the alpha-titanium alloy, AT2-2, appears to fulfill the specific requirements--low thermal conductivity, absence of temper brittleness, complete absence of magnetization and good weldability.[41] The Soviet design of the 2000 MW turbogenerator rotor shown in Figure 8 is based upon the usage of this alloy. Operating data for this design are given in Table 2.

TABLE 2. OPERATING DATA FOR THE TURBOGENERATOR DESIGN OF FIGURE 8[41]

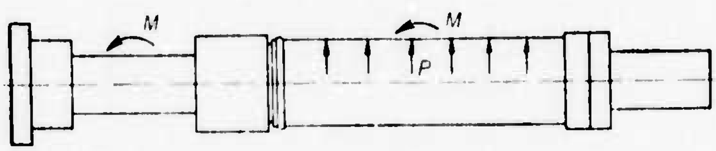
Turbo-generator power, MW	Method of cooling the rotor	Current density in the rotor winding, A/mm^2	Rotor weight, kg	Generator weight per unit of power, kg/kVA	Efficiency
2000	Extreme cooling, supercon-ductivity	116.0	47,000	0.196	99.390

The mechanical properties of the rotor material must be as good as those of similar 1000 MW generators, which, according to the authors, V. G. Danko, et al., are those given in Table 3.

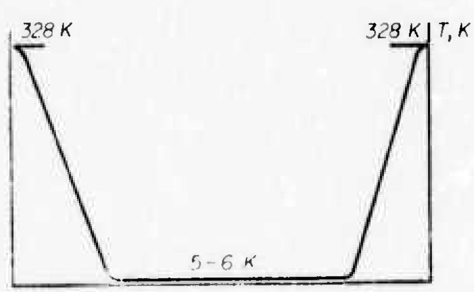


(a) Design of the turbogenerator rotor.

The length of the body of the rotor is 8000 mm; total length between the supports is 10,000 mm. The diameter of the body is 1260 mm. An inductor weighing 8-10 tons is placed inside the rotor.



(b) Sketch of the external loads on the rotor



(c) Temperature distribution over the length of the rotor.

The center of the rotor is maintained at 4-10 K. The low-temperature area is separated from the surrounding medium by an evacuated space.

FIGURE 8. SKETCH OF A SOVIET 2000 MW TURBOGENERATOR ROTOR WITH SUPERCONDUCTOR FIELD WINDINGS[41]

TABLE 3. REQUIRED MINIMUM MECHANICAL PROPERTIES OF ROTOR MATERIAL IN A 1000 MW TURBOGENERATOR[41]

Part	Yield strength, kg/mm^2	Tensile strength, kg/mm^2	Elongation, %	Reduction, %	Forging weight, kg
Rotor shaft	63	75	16	40	82,000
Nonmagnetic rings	90	98	20	35	2200 x 2

The following quoted excerpts, taken from the paper of Danko, et al. show in what manner, AT2-2, was selected:

> "The rotor is subjected to the action of forces from centrifugal force (the rate of rotation is 3000 rpm), torque, and temperature gradients, the total value of which reaches 45 kg/mm^2 both in the journals of the shaft and in the body of the rotor. A sketch of the external forces and the temperatures is shown in Figures [6(b) and (c)]. In addition, there is the possibility of the instantaneous action of torque from short circuits up to $5 \cdot 10^6$ kg-m. The presence of vibrations and reversing loads makes the operating conditions of rotor materials even more rigid."

> "An analysis of the operating conditions of a rotor with a superconducting excitation winding has shown that the most satisfactory properties are possessed by AT2-2 alloy.[42,43] Depending upon the method of treatment it has at 293 K a yield strength of 58-71 kg/mm^2 and an elongation of 22-25 percent, and at 4 K 107-140 kg/mm^2 and 20-26 percent. However, these figures were obtained on test samples cut from small bars."

> "The calculated weight of forgings of this alloy with a diameter of 1200-1300 mm and a length of 4000-10,000 mm is about 30 tons."[41]

References [41,42,43 and 44], which cover the Soviet development of the AT2-2 titanium alloy, do not give the compositions of the AT2-2 alloy test pieces investigated. The only composition available was that given in a 1971 Soviet

handbook on the low temperature mechanical properties of industrial nonferrous metals. [47] The handbook shows the alloy to be a Ti-2.5 percent Zr-1.3 percent Mo alloy*. The impurity limits given do not fall within the ELI (extra low impurity) range. It is conceivable that the impurity contents of the lots of AT2-2 alloys used in these experiments may have been lower than that permitted in Soviet Specification No. TS28T69-9.

A great deal of investigation has gone into the AT2-2 titanium alloy. Mechanical property data from a number of Soviet investigators are given in Tables 4, 5, 6 and 7. Comparisons are made with the Soviet standard comparison stainless steel Kh18N10T (US Equivalent, AISI 321) and with the lower nickel Soviet stainless steel, Kh21N5AG7 (a near equivalent to Armco's 21-6-9). Table 7 covers the mechanical properties of AT2, a modification of AT2-2. The Soviet literature indicates that the difference between the two is minor, but the exact nature of the difference is not known. In any case, the tensile properties for AT2-2 in Table 4 agree well with those given for AT2 in Table 7.

As indicated above, the principal US titanium alloy for these applications is an ELI 5Al-2.5Sn alloy. It also is an alpha titanium alloy, and has been used in cryogenic superconducting applications. As shown in Tables 4 and 5, the Soviets have also looked at the Ti-5Al-2.5Sn alloy (their VT5-1). It is stronger than AT2-2 at low temperatures, but its elongation, reduction in area and ratio of notched to unnotched tensile strength are appreciably lower. The latter ratio is a qualitative criterion of the capacity of the metal to redistribute the load at points of stress concentration. Thus, the higher the notched tensile strength in relation to that of the smooth specimens, the less probable is brittle failure and the more suitable the material for low temperature operation.

The impurity levels for the AT2-2 and VT5-1 alloys used in these experiments were not given. This omission is unfortunate, since impurities have a marked effect on low temperature ductility and toughness.

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*Soviet Specification No. TS28T69-9; Composition range, percent: Zr, 2.0-3.0; Mo, 0.8-1.8; Fe, 0.3 max, Si, 0.15 max, C, 0.10 max, N_2, 0.05 max, O_2, 0.15 max, and H_2, 0.01 max.

TABLE 4. MECHANICAL PROPERTIES OF SOVIET STAINLESS STEELS AND TITANIUM ALLOYS AT TEMPERATURES DOWN TO -269 C[43]

Material	Condition	Yield (0.2% offset), kg/mm^2				Tensile Strength, kg/mm^2				Elongation, %				Reduction in Area, %			
		20 °C	-196 °C	-253 °C	-269 °C	20 °C	-196 °C	-253 °C	-269 °C	20 °C	-196 °C	-253 °C	-269 °C	20 °C	-196 °C	-253 °C	-269 °C
Kh18N10T(a) US Equiv. AISI 321	Rod (d = 14 mm), as received	31	64	78	69	66	153	170	176	68	53	34	49	77	69	56	54
Kh21G7AN5(a) US Equiv. Armco 21-6-9	Rod (d = 16 mm), as received	45	118	142	158	80	164	173	184	64	54	20	30	76	66	23	36
Unalloyed Ti, VT1-1 (0.16% Fe; 0.045% Si; 0.014% C; 0.028% N; 0.0092% H) US Equiv. A-55	Bar, forged, annealed(c)	40	75	90	87	52	99	128	121	24	44	29	35	59	68	64	58
Titanium Alloy VT5-1 (0.25% Fe; 4.5% Al, 2.5% Sn) US Equiv. 5Al-2.5Sn	Bar, forged, annealed(c)	81	135	--	160	88	143	162	171	17	14	10	9	36	28	20	19
Titanium Alloy AT2-2(b)	Bar, forged annealed(c)	58	97	118	107	64	100	128	122	25	31	22	26	72	77	66	64

(a) Specimen Compositions (balance Fe):

	C	Si	Mn	S	P	Cr	Ni	Cu	Ti	N
Steel Kh18N10T	0.07	0.33	1.08	0.007	0.028	17.46	9.46	0.18	0.32	--
Steel Kh21G7AN5	0.07	0.45	0.92	0.012	0.08	21.05	5.63	--	--	0.21

(b) Composition Range Percent, Titanium Alloy AT2-2, according to Soviet Spec. TS28T69: -- Zr, 2.0-3.0, Mo 0.8-1.8; Bal Ti; Limit of impurities Fe, 0.3 max; Si, 0.15 max; C, 0.10 max, N_2, 0.05 max; O_2, 0.15 max; H_2, 0.01 max

(c) The heat treatment conditions for forged bars (12 mm square) were as follows: VT1-1 and AT2-2 annealed 30 min at 600 C; VT5-1 annealed 30 min at 800 C.

TABLE 5. COMPARISON OF NOTCHED-TENSILE TEST DATA FOR THE SOVIET STAINLESS STEELS AND THE TITANIUM ALLOY IN TABLE 4[43]

Strength characteristic	Testing temp., C	Stainless Steel Kh18N10T (US Equiv. AISI 321)	Stainless Steel Kh21G7AN5 (US Equiv. Armco 21-6-9)	Unalloyed Ti, VT1-1 (US Equiv. A-55)	Ti Alloy VT5-1 (US Equiv. 5Al-2.5Sn)	Ti Alloy AT2-2
Notched Tensile Strength(a), kg/mm²	20	91	150	98	169	211
	-196	169	--	171	188	194
	-253	155	216	185	158	201
	-269	--	--	192	--	--
Ratio $\frac{\text{Notched Tensile Strength}}{\text{Unnotched Tensile Strength}}$	20	1.39	1.89	1.92	1.76	1.91
	-196	1.11	--	1.715	1.23	1.94
	-253	0.91	1.24	1.52	0.92	1.57
	-269	--	--	1.50	--	--
Ratio $\frac{\text{Notched Tensile Strength}}{\text{Unnotched Yield Strength}}$	20	2.91	3.48	2.47	2.08	2.08
	-196	2.53	--	2.29	1.40	2.00
	-253	2.00	1.52	2.05	--	1.70
	-269	--	--	2.20	--	--

(a) Run on cylindrical specimens with ring notches; diam 4 mm at the notch, notch depth, 2 mm.

TABLE 6. MECHANICAL PROPERTIES OF TITANIUM ALLOY AT2-2[(a)] PLATE AND BAR AT LOW TEMPERATURES[44]

Form	Temp., C	Tensile Strength, kg/mm^2	Yield Strength (0.2% offset), kg/mm^2	Elongation, percent	Reduction in Area, percent	Mesnager Impact Strength, kgm/cm^2	Notched Tensile Strength, kg/mm^2	Ratio $\frac{\text{Notched Tensile Strength}}{\text{Unnotched Tensile Strength}}$
Plate	20	77.2	71.0	22.8	--	--	--	--
	-196	132	125.4	19.3	--	--	--	--
	-253	158	144.0	20.5	--	--	--	--
Bar	20	73.5-76.6	--	12.4-19.6	42.3-61.3	12.6-19.2	110-117	1.52
	-196	107.9-109.7	--	28-32	54.7-72	--	150-152.2	1.33
	-253	136-153	123-131	12.4-23.6	--	11.2-17.3	162-170	1.20

(a) Alloy heat treatment: heated to 600 C, cooled in air.

TABLE 7. MECHANICAL PROPERTIES OF STEEL Kh1810T (AISI 321) AND TITANIUM ALLOY AT2 AT LOW TEMPERATURES[42]

Material	Temp., C	Tensile Strength, kg/mm^2	Yield Strength (0.2% offset), kg/mm^2	Elongation, percent	Reduction in Area, percent	Mesnager Impact Strength, kgm/cm^2	Modulus of Elasticity, $kg/cm^2 x10^6$
Stainless Steel	20	60-133	25-120	10-73	55-72	5.5-32	2.07
Kh18N10T	-196	120-177	32-153	32-43	50-58	7-25	2.23
(US Equiv AISI 321)	-253	142-180	53-153	21-32	15-42	8-23	2.29
Titanium Alloy AT2	20	60-75	50-68	15-24	49-55	8-18	1.07
	-196	95	85	25	72	11	1.22
	-253	120	103	18	--	9	1.25

Potential Nickel Alloys for Cryogenic Applications in Superconducting Electrical Machinery

Soviet nickel alloy KhN63M9B2Yu* was developed for use in welded structures operating at -253 to +750 C.[48] The strength of weldments is reported to be 90 percent of the strength of the base metal. For low temperature operation the limiting values of the niobium and iron constituents appear to be 3 and 5 percent respectively. As the mechanical property values in Table 8 show, the alloy has a fairly high notched to unnotched tensile ratio which does not vary appreciably with temperature.

TECHNICAL FORECAST ANALYSIS

On the basis of what is published in the literature, the Soviets appear to be temporarily ahead of the West in the application of stainless steel and titanium alloys for constructional members in cryogenic applications relating to superconducting electrical machinery. The Soviet lead probably is temporary, since their development of new alloys does not appear to be continuing; it is just a case of the Soviets adopting alloys that do not seem to have been used as yet in the West.

It would also appear from the Soviet literature that what appears to be their best stainless steel (21Cr-16Ni-6Mn-N2) for this application may be preferred to the AT2-2 titanium alloy. Recent Soviet publications emphasize the usefulness of the 21-16-6-N stainless steel; on the other hand, there has been no mention of the AT2-2 alloy since October 1970.

Visitors to the USSR have noted the fact that Soviet laboratories doing developmental work on cryogenics related to superconductivity are not so well equipped as are corresponding US laboratories. There is a feeling that Soviet publications in this area indicate that more is being done than is actually the case. Nevertheless, some high quality research and development is being done. Since Soviet

*Nominal composition, percent: 18Cr, 9Mo, 2.5-3Nb, 1.5Al, 5Fe, balance Ni (The alloy probably also contains about 0.005 percent boron).

TABLE 8. HEAT TREATMENT AND MECHANICAL PROPERTIES OF SOVIET NICKEL-BASE ALLOY, KhN65M9B2Yu AT 20, -253 AND 750 C[48]

Heat treatment	at 20 C: Tensile Strength, kg/mm2	at 20 C: Yield Strength (0.2% offset), kg/mm2	at 20 C: Elongation percent	at 20 C: Reduction of Area percent	at 20 C: Mesnager Impact Strength kg/mm2	at 20 C: Ratio of Notched Tensile Strength / Unnotched Tensile Strength	at -253 C: Tensile Strength kg/mm2	at -253 C: Yield Strength (0.2% offset), kg/mm2	at -253 C: Elongation, percent	at -253 C: Reduction of Area, percent	at -253 C: Mesnager Impact Strength kg/mm2	at -253 C: Ratio of Notched Tensile Strength / Unnotched Tensile Strength	Strength after 1 hr at 700 C kg/mm2	after 15 min at 700 C and 1% strain, kg/mm2
Bars 55 mm in diameter														
Quench 1100 C 1 h, air	85	40	60	53	15	--	--	--	--	--	10.5	--	--	--
Quench 1100 C 1 hr, air + age 700 C 15 h	104	55	19	45	8	1.44	138	81	52	33	5	1.4	64	50
Plate 1.5 mm thick														
Quench 1050 C 6 min air	90	54	--	46	--	1.3	--	--	--	--	--	1.3	--	--
Quench 1050 C 6 min air + age 700 C 15 h	109	73	--	34	--	--	153	112	--	19	--	1.1	70	50
Welded plates 1.5 and 5 mm thick														
EP367 filler wire Quench 1100 C, 1 h 1 h air + age 700 C, 10 h	99	--	--	--	5	--	119	--	--	--	6	--	--	--

efforts to develop construction material for cryogenic applications relating to superconduction parallel those of the US, and also since there appears to be very good communication between the two countries in this field, it would appear that for the next five years, at least, they will remain pretty much on a par in this particular area. The present slight advantage of the USSR is expected to be short lived.

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